

# Bodipy-backboned polymers as electron donor in bulk heterojunction solar cells†

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**Bodipy-based polymers, which possess a high absorption coefficient with a bandgap of  $\sim 1.6$  eV, have been used as electron donor in solution-processed bulk heterojunction (BHJ) solar cells containing PCBM as acceptor. A power conversion efficiency (PCE) of  $\sim 2\%$  has been achieved with  $V_{oc}$  of  $\sim 0.8$  eV and  $J_{sc}$  of  $\sim 4.8$  mA cm<sup>-2</sup>.**

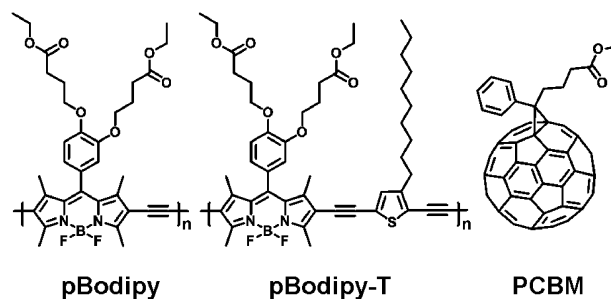
Solution processed bulk heterojunction (BHJ) polymer/fullerene solar cells have attracted much attention in the past decade for their substantial future prospects as low-cost 3rd generation photovoltaic (PV) technology.<sup>1</sup> Conjugated polymers have the advantage of high absorption coefficients for efficient light harvesting and exciton generation in thin films. In addition, composites of polymers and fullerene form bicontinuous nanophase morphology for efficient charge separation and transport.<sup>2</sup> For instance, the most investigated poly-(3-hexylthiophene) (P3HT)/[6,6]-phenyl C<sub>61</sub> butyric acid methyl ester (PCBM) system is able to harvest most of the photons of the solar spectrum from 400 nm to 675 nm and generate nanophase separation between P3HT and PCBM with domain sizes of 10–20 nm upon thermal or solvent annealing, resulting in power conversion efficiencies (PCEs) of 4–5%.<sup>2</sup> However, P3HT is not the ideal polymer as it has a relatively large bandgap (1.85 eV) and its high-lying highest occupied molecular orbital (HOMO) limits the  $V_{oc}$  of P3HT/PCBM devices.

To increase the light-harvesting abilities of polymers for improving BHJ device efficiencies, new low bandgap polymers with  $E_g$  down to *ca.* 1.4 eV have been synthesized.<sup>1d,3</sup> One successful approach to low bandgap materials involves the donor–acceptor copolymers, in which electron-rich units and electron-deficient moieties are integrated into a single conjugated polymeric system. For example, alternating copolymers containing carbazole/benzothiadiazole,<sup>3c</sup> bithiophene/diketopyrrolopyrrole,<sup>3h</sup> and benzo[1,2-*b*:4,5-*b'*]dithiophene/thieno[3,4-*b*]thiophene<sup>3j</sup> units have demonstrated efficiencies of 4–7% when paired with [6,6]-phenyl C<sub>71</sub> butyric acid methyl ester in BHJ solar cells.

Here we explore the use of borondipyrromethene (Bodipy)-backboned polymers<sup>4</sup> (pBodipy and pBodipy-T in Fig. 1) as donor materials for PV application. Unique features of Bodipy dyes include their high absorption coefficients and high luminescence quantum yields, delocalized molecular orbitals as well as excellent photochemical and thermal stability.<sup>5</sup> These characteristics suggest that Bodipy-backboned polymers may be useful in PV applications. Recently, a few organic solar cells using small molecular Bodipy derivatives as electron donor and PCBM as acceptor have been reported affording PCE of up to 1.7% for multi-Bodipy dyes/PCBM solar cells.<sup>6</sup> In this study, we have incorporated the Bodipy moiety into the conductive polymer backbone. We report the optoelectronic properties of these Bodipy-backboned polymers and their performance in solution processed BHJ solar cells.

Fig. 2 shows the UV-Visible absorption spectra of the thin films prepared by spin coating the polymers from chloroform solutions. The UV-Visible spectrum of a P3HT film spin coated from chlorobenzene solution is also plotted to enable the direct comparison of the optical properties of the polymers. As a result of molecular stacking in the solid state, the absorption maxima for the thin films of pBodipy and pBodipy-T are at 721 nm and 692 nm respectively; these values are red-shifted by  $\sim 60$  nm from the corresponding absorptions in dichloromethane solutions.<sup>4</sup> The optical band gaps for both polymers are estimated at  $\sim 1.6$  eV (see Table 1). Noticeably, the light absorption of the Bodipy polymers is much broader and stronger than that of P3HT in the range of 300–800 nm, leading to significantly improved overlap with the solar spectrum. Both the low optical bandgap and the high extinction coefficient ( $\sim 10^5$ /cm) of the Bodipy polymers suggest that these materials could be useful donor materials for PV application.

Cyclic voltammetry (CV) measurements were carried out to determine the HOMO and lowest unoccupied molecular orbital (LUMO) levels of these polymers. The CV curves are



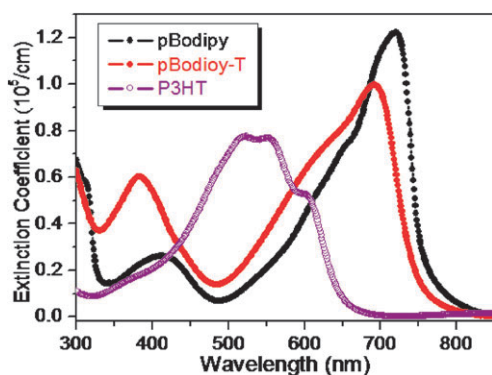
**Fig. 1** Structures of Bodipy-backboned polymers (pBodipy and pBodipy-T) and PCBM.

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**Fig. 2** UV-Vis absorption spectra of pBodipy and pBodipy-T in films.

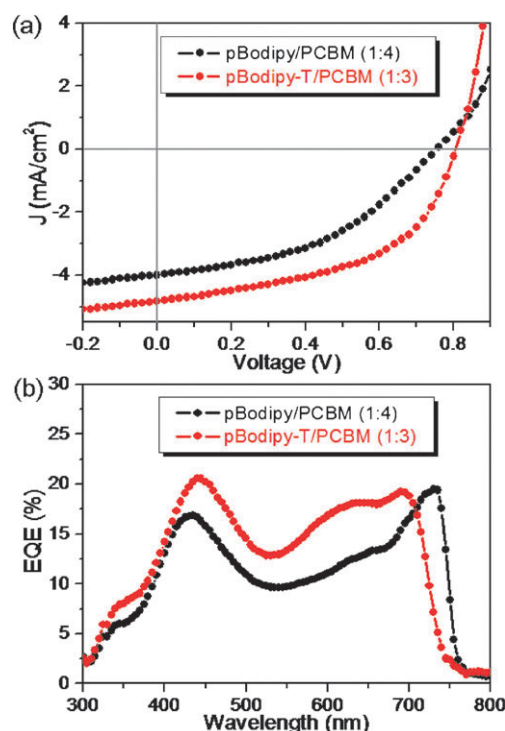
**Table 1** Optical/electrochemical properties of pBodipy and pBodipy-T

Polymer	$E_{\text{ox}}^a/\text{HOMO}^b$	$E_{\text{red}}^a/\text{LUMO}^b$	$E_{\text{g}}^{\text{ec}}/\text{eV}$	$E_{\text{g}}^{\text{opt}}/\text{eV}$
pBodipy	0.47/5.58	-1.38/3.73	1.85	1.61
pBodipy-T	0.34/5.45	-1.40/3.71	1.74	1.65

<sup>a</sup> Potentials determined by cyclic voltammetry in 0.10 M  $\text{Bu}_4\text{NPF}_6\text{-CH}_3\text{CN}$  vs. ferrocene/ferrocene<sup>+</sup>. <sup>b</sup> Assuming the electrochemical potential of ferrocene/ferrocene<sup>+</sup> = 5.10 eV vs. vacuum.

provided in the ESI† (Fig. S1). The HOMO and LUMO levels as well as the electrochemical bandgap ( $E_{\text{g}}^{\text{ec}}$ ) were determined from the oxidation and reduction potentials of the polymers; these values are summarized in Table 1. We found that the insertion of thiophene units into the backbone of the pBodipy polymer changes the HOMO level from 5.58 eV to 5.45 eV. In contrast, the LUMO level remains essentially unchanged. This implies that the HOMO levels are mainly affected by the donor units in the polymer backbone, while the LUMO levels ( $\sim 3.7$  eV) are primarily controlled by the Bodipy moieties. Given that the LUMO of PCBM is at  $\sim 4.1$  eV, the energy difference between LUMOs of these polymers and PCBM is about 0.4 eV, which should be sufficient for exciton splitting and charge dissociation.<sup>1b</sup>

BHJ polymer solar cells were fabricated using PCBM as the electron acceptor with the device structure: ITO/PEDOT:PSS/active layer (polymer:PCBM)/Al. Table 2 summarizes the device characteristics of the polymer solar cells with different weight ratios of PCBM under 100  $\text{mW cm}^{-2}$  AM 1.5 G solar illumination. The optimal active polymer/PCBM layer thickness is around 70 nm. The best solar cells were obtained using 1:4 and 1:3 ratios of pBodipy and pBodipy-T polymer to PCBM, respectively. Fig. 3(a) shows the current density–voltage ( $J$ – $V$ ) characteristics of the best solar cells. The open circuit voltage ( $V_{\text{oc}} \sim 0.8$  V) achieved for both polymer/PCBM composites is 0.2 V higher than that obtained with P3HT/PCBM BHJ cells. This is consistent with the fact that the HOMO levels of these polymers are lower than that of P3HT by 0.2–0.4 eV.<sup>1c</sup> The pBodipy-T device showed higher short circuit current density ( $J_{\text{sc}}$ ) and fill factor (FF) than the pBodipy device, leading to efficiencies of 2.0% vs. 1.3%. Unfortunately, the current density is still much lower than that of the state-of-the-art polymer/fullerene systems.<sup>2,3</sup>



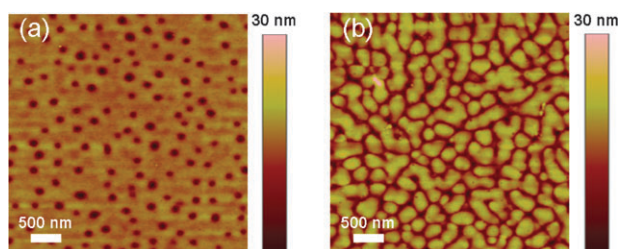
**Fig. 3** (a)  $J$ – $V$  characteristics of solar cells with the configuration of ITO/PEDOT:PSS/active layer (polymer:PCBM)/Al under 100  $\text{mW cm}^{-2}$  AM 1.5 G illumination. The weight ratio of polymer/PCBM is 1:4 and 1:3 for pBodipy/PCBM and pBodipy-T/PCBM, respectively. (b) External quantum efficiency spectra of the optimized devices as a function of wavelength, measured at 0 V.

**Table 2** Device characteristics of Bodipy-backed polymer solar cells with different weight ratios of PCBM under 100  $\text{mW cm}^{-2}$  AM 1.5 G simulated illumination

Active layer (wt/wt)	$V_{\text{oc}}/\text{V}$	$J_{\text{sc}}/\text{mA cm}^{-2}$	FF	PCE (%)
pBodipy:PCBM (1:2)	0.73	-3.21	0.39	0.9
pBodipy:PCBM (1:3)	0.81	-3.39	0.45	1.2
pBodipy:PCBM (1:4)	0.76	-4.00	0.43	1.3
pBodipy-T:PCBM (1:2)	0.77	-4.20	0.50	1.6
pBodipy-T:PCBM (1:3)	0.80	-4.82	0.51	2.0
pBodipy-T:PCBM (1:4)	0.81	-4.20	0.54	1.8

In order to understand the origins of the low current density, we carried out external quantum efficiency (EQE) measurements. Fig. 3(b) shows the EQE spectra of the optimized solar cells, which display light harvesting up to 770 nm. The short wavelength region around 450 nm is mainly contributed by PCBM, the longer wavelength region by the polymers. The higher  $J_{\text{sc}}$  of the pBodipy-T device compared to the pBodipy device is reflected in the higher EQE values over the entire spectrum. However, it is clear that the low (less than 20%) EQE values of both polymer/PCBM cells are responsible for the low  $J_{\text{sc}}$  (4–5  $\text{mA cm}^{-2}$ ). Further, we find that the low EQE values correlate to two important factors: (i) the non-ideal nanoscale phase separation between the polymers and PCBM, and (ii) the low hole mobilities of the polymers as explained below.

Tapping mode atomic force microscopy (AFM) measurements were carried out on the blend films to investigate film morphology. AFM images of the active layer films (Fig. 4)



**Fig. 4** Tapping mode AFM topography images of the polymer blend of (a) pBodipy/PCBM (1 : 4) and (b) pBodipy-T/PCBM (1 : 3). Image size is  $4 \times 4 \mu\text{m}^2$ .

show coarse phase separation with domain sizes in the range of hundreds of nanometres with root-mean-square (rms) roughness of 2.55 nm for the pBodipy/PCBM (1 : 4) film and 4.33 nm for pBodipy-T/PCBM (1 : 3) film. This domain size is much larger than the exciton diffusion length of *ca.* 10 nm<sup>1b,2</sup> favoring recombination and low charge carrier generation at the polymer/PCBM interfaces with a concomitant loss of photocurrent. Therefore, further improvement in device performance would require significant enhancement in morphology control to reduce domain size to *ca.* 20 nm.

The hole mobilities of the polymer neat films and polymer/PCBM blends were also measured in the dark using the structure: ITO/PEDOT:PSS/active layer/Au with an active film thickness of *ca.* 200 nm. Mobility values were calculated from current–voltage characteristics based on the space charge limited current model.<sup>7</sup> By assuming a dielectric constant of 3.0 for the active films, a hole mobility of  $1.7 \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  is obtained for the pBodipy:PCBM (1 : 4) blend film and  $4.4 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for the pBodipy-T:PCBM (1 : 3). For polymer neat films, we found hole mobilities of  $1.6 \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $3.0 \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for pBodipy and pBodipy-T, respectively. Therefore it is likely that the higher hole mobility of the pBodipy-T blend device leads to the higher observed  $J_{\text{sc}}$  and FF values. Nevertheless, these mobilities are lower than for other systems that have been reported<sup>2,3</sup> and likely limit the overall performance of these devices. Polymers incorporating high hole conducting donor units such as carbazole,<sup>3i</sup> and benzo[1,2-*b*:4,5-*b'*]-dithiophene<sup>3j</sup> with Bodipy moieties would lead to higher  $J_{\text{sc}}$  and FF.

In summary, we have demonstrated efficient BHJ polymer/PCBM solar cells with Bodipy-backboned polymers (pBodipy and pBodipy-T) as electron donor. The low bandgap and high extinction coefficient of these polymers afford efficient light harvesting of the solar spectrum up to  $\sim 1.6 \text{ eV}$ . CV results suggest that these polymers have an optimal energy level

alignment for charge separation when paired with PCBM, and the deep HOMO levels result in the high  $V_{\text{oc}}$  of 0.8 V. While the efficiency of 2% is among the highest reported so far for dye-based donor materials,<sup>3h,6,8</sup> it is clear that improvements in morphology control as well as structural modification are needed to draw full benefit from this type of polymers.

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